

<b>REPORT DOCUMENTATION PAGE</b>				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.					
<b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b>					
1. REPORT DATE (DD-MM-YYYY) 24-03-2001		2. REPORT DATE final report		3. DATES COVERED (From - To) Mar 2000-Jan 2001	
4. TITLE AND SUBTITLE Deposition of Undercooled Liquid Ceramics				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER N00014-00-1-0442	
				5c. PROGRAM ELEMENT NUMBER	
				5d. PROJECT NUMBER	
6. AUTHOR(S) Hofmeister, William and Wehrmeyer, Joseph				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Steve Smartt, Director of Sponsored Research 512 Kirkland Hall Vanderbilt University; Nashville, TN 37240				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Ralph F. Wachter Office of Naval Research Ballston Centre Tower One 800 North Quincy Street; Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT unrestricted <div style="float: right; text-align: right; font-size: 2em; font-weight: bold; margin-top: 10px;">             20010405 011           </div>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The objective of the research is to show that ceramic particles can be melted in flight, undercooled in flight, and impacted on a substrate to form a thick film. It is further hypothesized that with adequate process control, deposits of high temperature ceramics can be created on heat sensitive substrates, e.g., hybrid electronic structures. The approach is to flow powders in a gas stream through a region of high photon flux to melt the powders, cool the molten particles by radiation, convection and conduction during free flight, and control phase selection and droplet spreading on a substrate by modeling, in-process diagnostics, and metallographic examination of the deposits. The primary application of this process is for the sealing of hybrid ceramic bio-implantable devices, such as pacemakers. Ceramic pacemakers have communication capabilities, integrated feedthroughs, and are MRI and biologically compatible. There is presently no known biocompatible method for sealing these hybrid devices. Other applications include the formation of thick films at high rates for ceramic superconducting tapes and wires, ceramic superconducting coatings for electromagnetic shielding, thermal barrier coatings on heat sensitive substrates, micro coatings for MEMS components, and ceramic joining.					
15. SUBJECT TERMS undercooling, layered manufacturing, bio-materials, ceramics, superconductors, hybrid devices					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	UU		19a. NAME OF RESPONSIBLE PERSON William Hofmeister
					19b. TELEPHONE NUMBER (Include area code) 615-322-7053

## Final Report

### Deposition of Undercooled Liquid Ceramics March 24, 2001

---

#### Principal/co-Principal Investigator.

- \* PI/co-PI Name(s): William Hofmeister / Joseph Wehrmeyer
  - \* PI Institution: Vanderbilt University
  - \* PI Phone Number: 615-322-7053
  - \* PI Fax Number: 615-322-3202
  - \* PI E-mail Address: hof@vuse.vanderbilt.edu
  - \* PI URL Home Page: <http://www.vuse.vanderbilt.edu/~aesinfo/hofmeist.htm>
  - \* Grant/Contract Number: N00014-00-1-0442
  - \* Period of Performance: 03/15/00 - 1/30/01
- 

#### Project Attributes.

- \* Number of refereed papers/book chapters published: 0
  - \* Number of refereed papers/book chapters to appear: 0
  - \* Number of books published: 0
  
  - \* Number of unrefereed reports and other articles: 0
  - \* Number of project presentations: 0
  
  - \* Number of patents granted and software copyrights: 0
  - \* Number of patents filed but not yet granted: 0
  
  - \* Number of graduate students supported  $\geq$  25% of full time: 0
  - \* Number of post-docs supported  $\geq$  25% of full time: 0
  - \* Number of minorities supported: 0
- 

#### Summary of Objectives and Approach.

The objective of the research is to show that ceramic particles can be melted in flight, undercooled in flight, and impacted on a substrate to form a thick film. It is further hypothesized that with adequate process control, deposits of high temperature ceramics can be created on heat sensitive substrates, e.g., hybrid electronic structures.

The approach is to flow powders (individually or en masse) in a gas stream through a region of high photon flux (a laser beam) to melt the powders, cool the molten particles by radiation, convection and

conduction during free flight, and control phase selection and droplet spreading on a substrate by modeling, in-process diagnostics, and metallographic examination of the deposits.

The primary application of this process is for the sealing of hybrid ceramic bio-implantable devices, such as pacemakers. Ceramic pacemakers have communication capabilities, integrated feedthroughs, and are MRI and biologically compatible. There is presently no known biocompatible method for sealing these hybrid devices. Other applications include the formation of thick films at high rates for ceramic superconducting tapes and wires, ceramic superconducting coatings for electromagnetic shielding, thermal barrier coatings on heat sensitive substrates, micro coatings for MEMS components, and ceramic joining.

---

### **Summary of Technical Progress.**

A process simulation was developed, and experiments in heating and melting powders with various light sources were carried out. Powder delivery through a laminar flow nozzle was accomplished and the flow rates, particle velocities, and dispersion of the particle stream were measured. Samples from experiments with a 4kW laser diode source were examined in a scanning electron microscope. Apparatus was constructed to allow manipulation of the particle stream with a robot arm, and deposits of alumina and high temperature superconductors were produced.

A summary with pictures and movies is available in Power Point: "deposition of undercooled liquid ceramics final report.ppt".

**Powder heating** - Heating sources such as a quartz lamp, nichrome wire, laser diodes, Nd:YAG laser, 4kW diode laser, and 3 kW CO<sub>2</sub> laser were examined. The former sources do not have enough fluence to melt alumina powders in flight, but are useful for preheating powder streams. Testing was accomplished with a Pt-Rh thermocouple placed in the powder heating area. The nichrome wire heater was deemed the best for heating up to 1000C where the powder stream is still contained in a quartz tube. Above this temperature powders tend to stick in the tube, and further heating must be done in the free (uncontained) stream. A 45 watt three bar diode laser was tested with diffuse reflectors of various diameters. The temperature reached by the thermocouple was inversely proportional to the area (diameter) of the reflector. Various lens/reflector combinations were tested with a 150W Nd:YAG laser as well. The Nd:YAG laser with a cylindrical lens and reflector was capable of melting stationary powders, however, the 4 kW source was necessary to melt moving particles in cold gas streams. Melting experiments using the 4 kW diode laser were carried out on powders from 45-109 microns in diameter, at 4kW and velocities up to 10 ms<sup>-1</sup>. Four different powders were tested, two high purity grades of alumina, one low (96%) purity grade, and high temperature superconductors. The results of all the above experiments were used to tune the process simulation. In addition, similar powders were tested using a 3kW CO<sub>2</sub> laser at University of Tennessee Space Institute in Tullahoma, TN.

**Nozzle testing** - Because the energy absorbed by the sample in an optical beam is proportional to the residence time, it is important to propel particles at as low a velocity as possible for melting. The design trade-off is the velocity required to spread the droplet on a substrate. A one mm i.d. pipette was tested with powders from 50-70 microns in diameter at 20 ms<sup>-1</sup>. At a 4 cm distance, less than 10% of the powder fell outside a 4 mm diameter. This design is considered sufficient for initial tests.

Deposits - It is evident from the 4 kW laser tests that a multi-stage heating apparatus is necessary to melt alumina at sufficient velocity to form good coatings. The deposits formed with the lower purity alumina were agglomerations of spheres, except where some portion of the optical beam was directed on the deposit. In these cases, monolithic deposits were created. The lower melting temperature and higher absorptivity of the ceramic superconductors allowed melting in the 4 kW beam and thick film deposits were generated. These experiment were repeated with the 3 kW CO<sub>2</sub> laser. This laser showed better absorptivity, but had less total power. Results were similar.

Summary - The high temperature superconductors show good promise for thick film deposition. Higher temperature ceramics, such as alumina will require about twice the power in the optical beam, i.e. 8kW, for deposition to be successful.

---

#### Transitions and DOD Interactions.

Contacted Harold Weinstock AFRL/AFOSR concerning fabrication of superconducting films.  
Contacted Don Gubser and M.A. Imam at NRL concerning superconducting deposits.

---

#### Current Students and Recent Graduates Supported by ONR.

1. Name: Blythe Gore
  - + US Citizen/Permanent Resident: citizen
  - + Thesis: none
  - + Graduated: scheduled to graduate from Northwestern May, 2001
  - + Home Page:
  - + Job: Ms. Gore was employed as a summer undergraduate worker

---

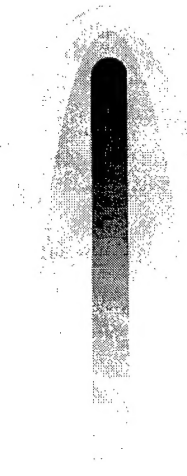
#### Related Research Projects.

Microgravity Processing of Oxide Superconductors (NAG8-1275, end date May 31, 2000). This project is related because of the emphasis on controlling phase selection via undercooling and splat quenching. High Speed Thermal Imaging for Process Development and Control (Sandia National Laboratory, contract BD-0123) is related because of the work with in-process thermal imaging and control of laser processes.

Superconductor deposits on textured substrates were sent to Amit Goyal at Oak Ridge National Laboratories for texture analysis in conjunction with the RABITS program.



# *deposition of undercooled liquid ceramics*



William Hofmeister

Department of Chemical Engineering

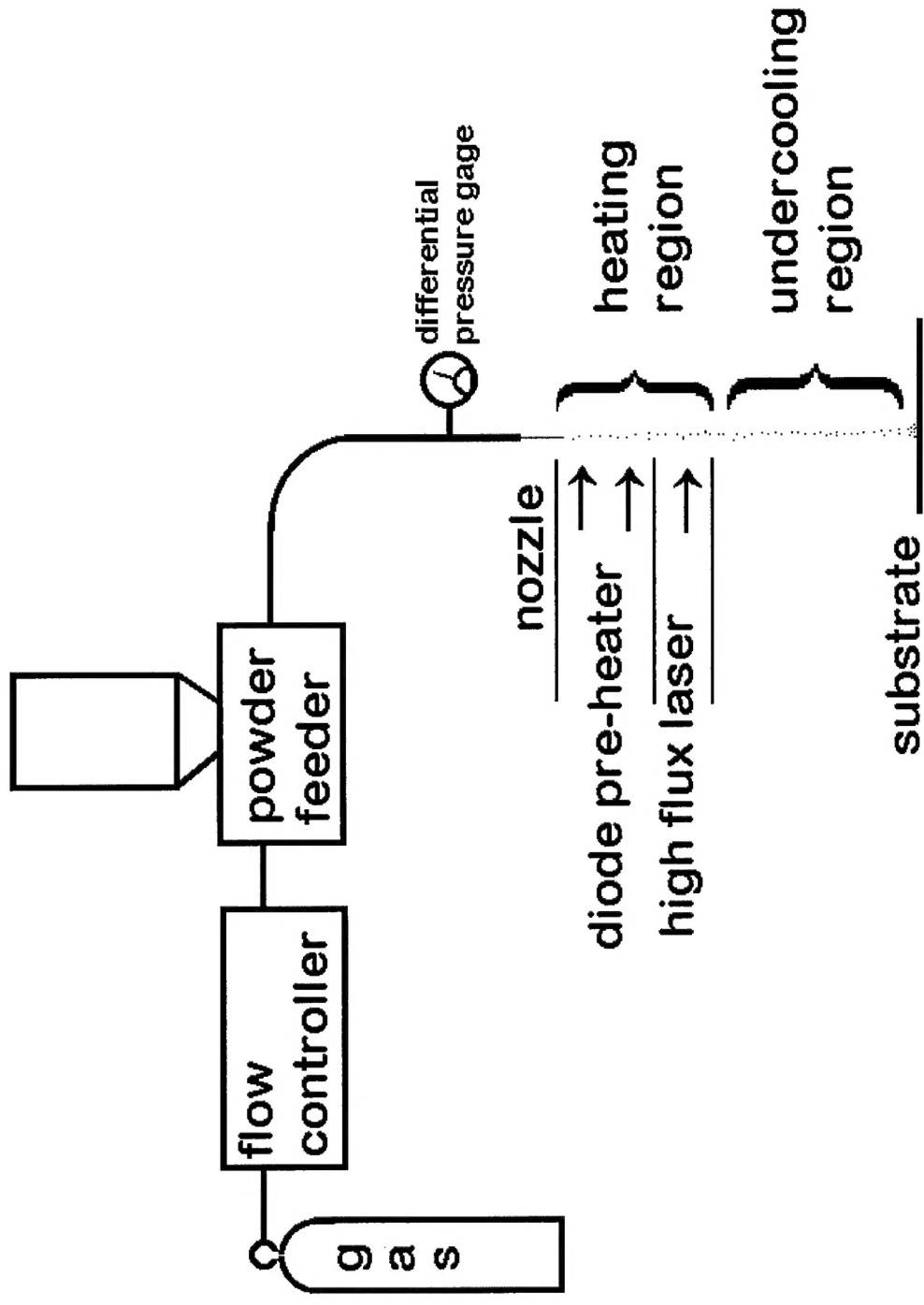
Joseph Wehrmeyer

Department of Mechanical Engineering

Vanderbilt University

ONR grant number N00014-00-1-0442

# *Schematic of ceramic deposition technique*



# *Advantages of Undercooled Liquid Ceramics*

- Undercooling gives some control of phase selection
  - Peritectic materials
  - *In situ* nanostructures
- Viscosity increase aids droplet spreading
- Deposit on heat sensitive substrates
- Texture possible

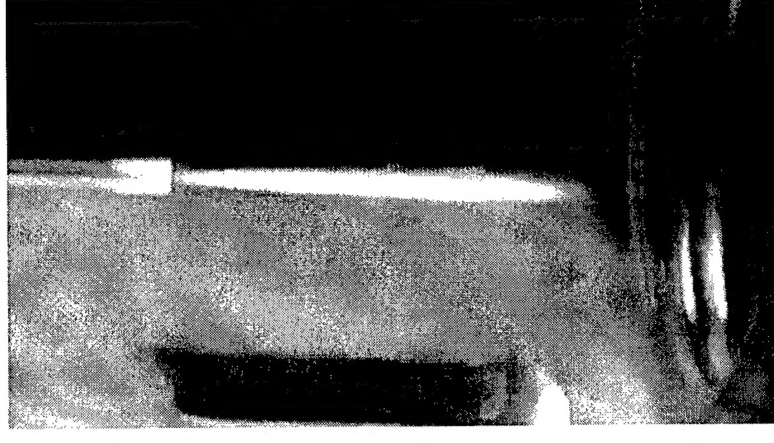
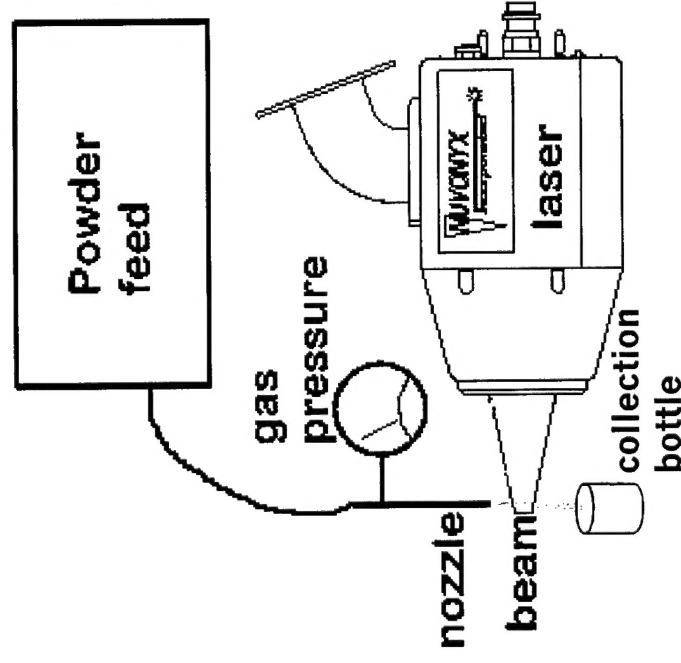
# *comparison with other free form ceramic deposition techniques*

- |   | <u>3D printing/ Robocasting slurries</u>  | <u>Undercooled Liquids</u>   |
|---|---|--|
| • | <ul style="list-style-type: none"><li>– Require heat treatment</li><li>– Polycrystalline</li></ul>                            | <ul style="list-style-type: none"><li>used as-deposited</li><li>possible texture/epitaxy</li></ul>                                 |
| • | Selective Laser Sintering <ul style="list-style-type: none"><li>– Porous structures</li></ul>                                 | solidification to full density   |
| • | SALD <ul style="list-style-type: none"><li>– Vapor decomposition is slow</li><li>– Features controlled by beam size</li></ul> | <ul style="list-style-type: none"><li><math>&gt;10^3</math> faster deposition</li><li>features controlled by powder size</li></ul> |

# *Applications of Undercooled Liquid Ceramics*

- Hermetic sealing of ceramic enclosures for implantable devices (Medtronic, Inc.)
  - Pacing and neurological devices
  - Bio-inert, MRI compatible, integrated feedthroughs, telemetry
- Thick films of high temperature superconductors
- Free-form fabrication of insulators
- Ceramic welding
- Thermal barrier coatings

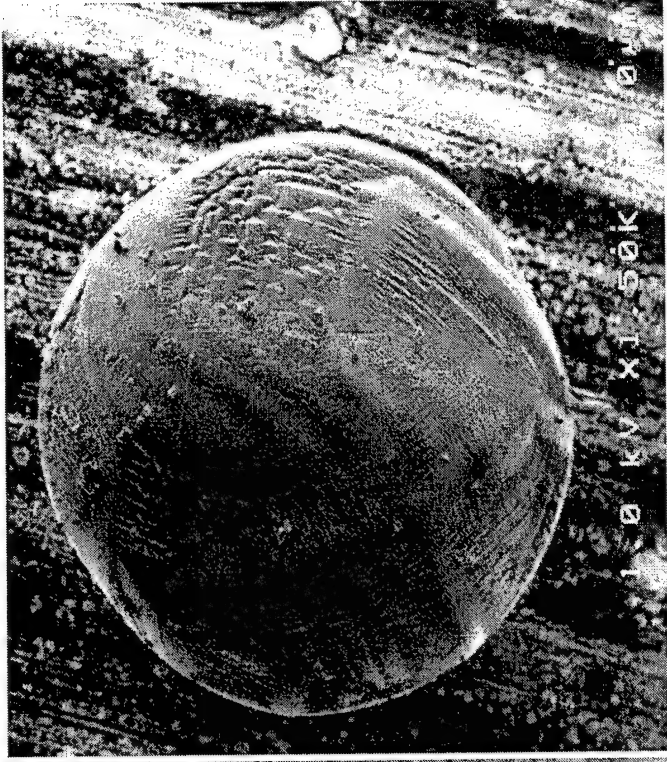
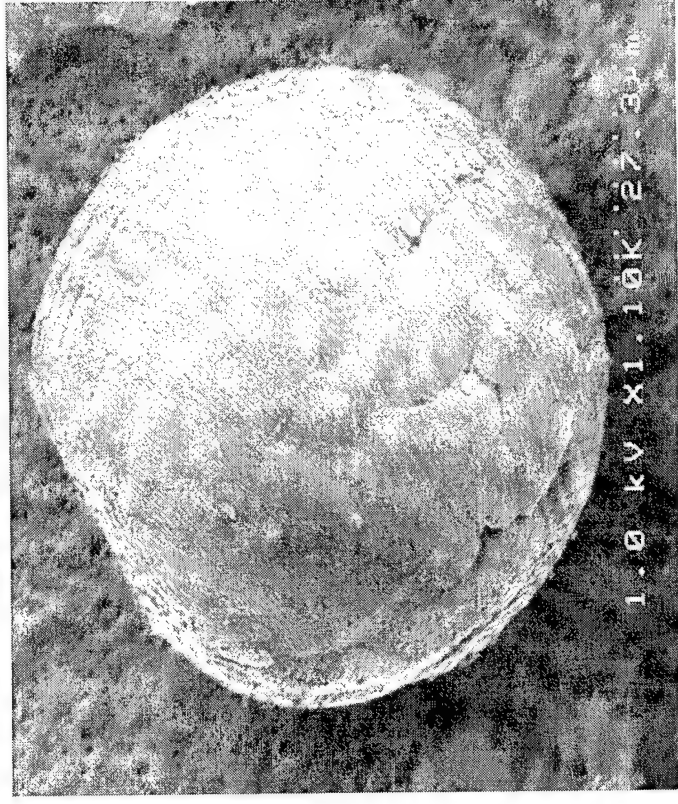
# *Powder melting experiments*



Powders were collected as a function of particle velocity to determine residence time necessary for melting.

[Click picture to run movie](#)

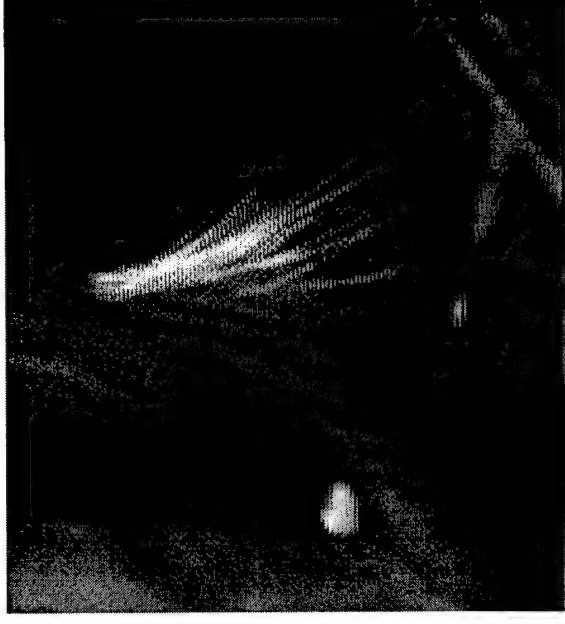
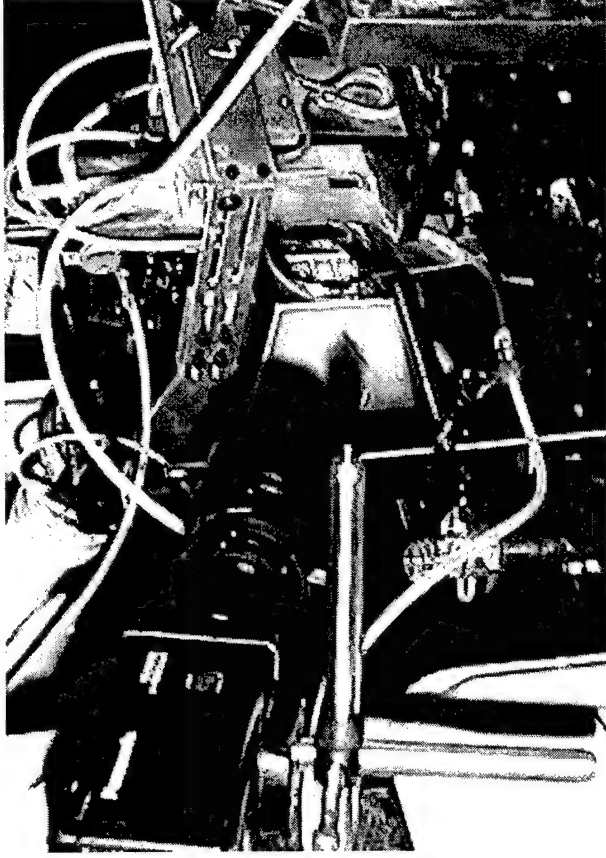
# *Microstructure of melted alumina*



Melted particles are evident by the spherical shape and dendritic or faceted/dendritic structures. (velocity =  $5\text{ms}^{-1}$ , power =  $4\text{kW}$ )



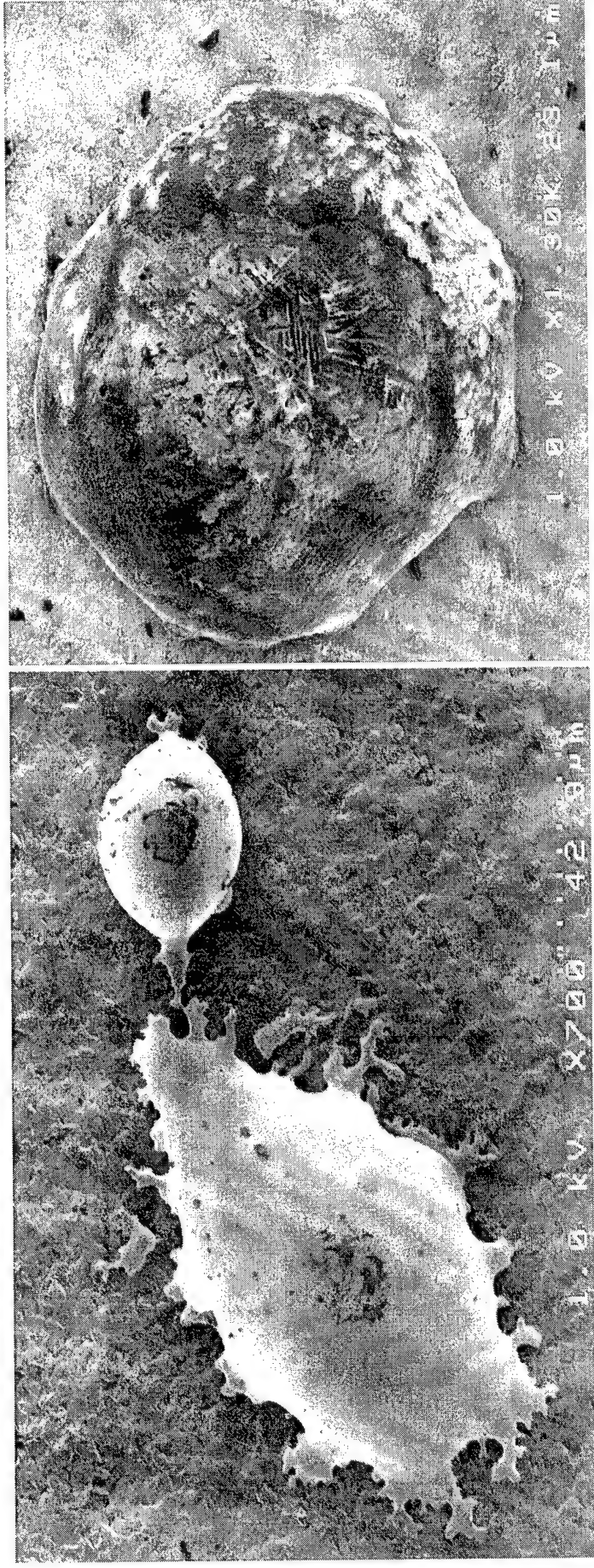
# *Substrate deposition*



[Click picture to run movie](#)

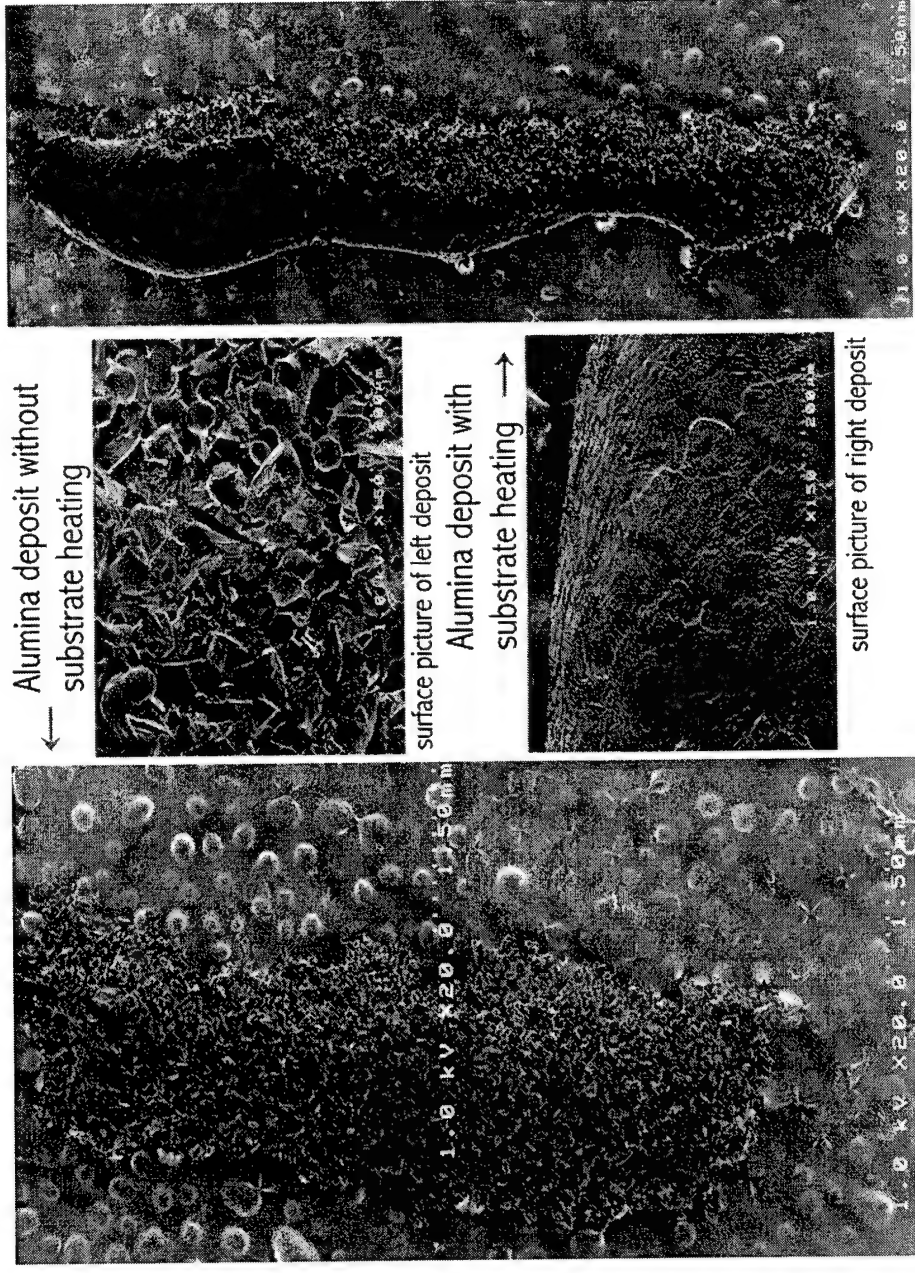
The Nuvonyx 4kW diode laser is shown mounted to a robot arm. The robot was used to manipulate the laser and deposition stream as shown in the movie.

# *Splats on substrates*



These alumina particles were impacted on a high purity alumina substrate at a velocity of  $5 \text{ ms}^{-1}$ . The velocity is too low for adequate spreading of droplets. The 4kW source is insufficient to melt alumina at higher velocities.

# *Alumina line builds*



The alumina line deposit on the left was shielded from the beam and shows that the particle stream contains un-melted particles. The deposit is a loose aggregate of melted spheres and un-melted particles. The right deposit was exposed to a low energy portion of the laser beam so that impacting particles are melted on the surface for a smooth finish. (4 kW, 5 ms<sup>-1</sup>)

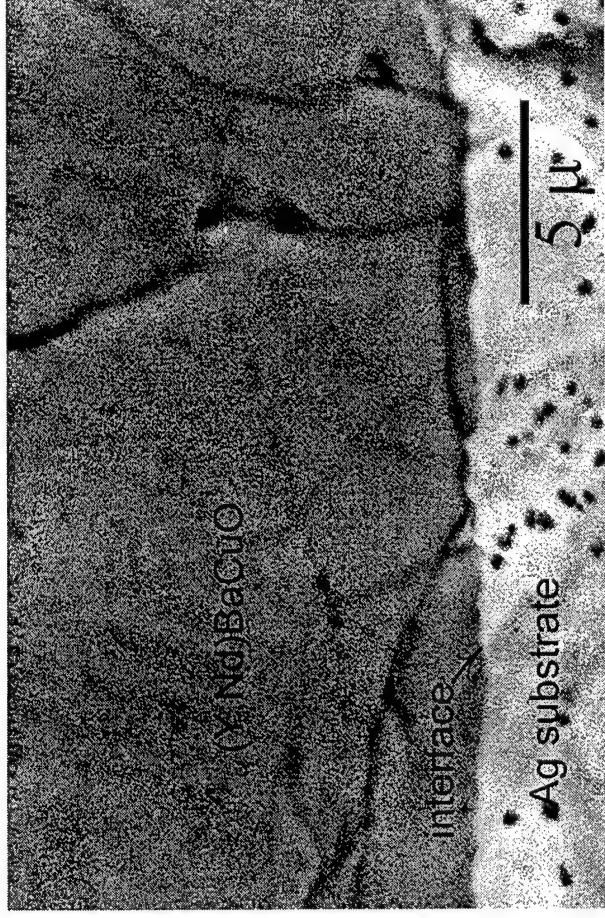


# *high temperature superconductor layer deposition*

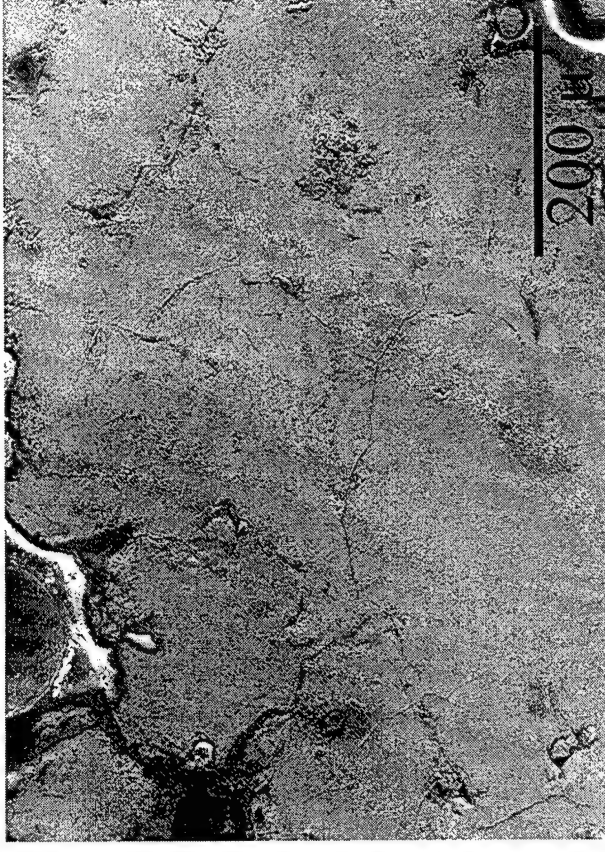


The high temperature superconductor  $\text{Y}_{0.3}\text{Nd}_{0.7}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  has a lower melting temperature and better absorptivity than alumina. The left deposit was 2 mm below the laser beam, the right was 8 mm below. The velocities were  $7 \text{ ms}^{-1}$  and  $9 \text{ ms}^{-1}$ , respectively.

# *Microstructures of HTS deposits*



This cross-section shows a superconductor deposit on a polycrystalline silver substrate. The deposit is single phase, tetragonal 123.



This is a section from a monolythic superconductor deposit 4 cm x 1 cm x 0.5 cm. The deposit is mostly 123 phase with some BaCu oxides.

# *Micron sized deposits*



A pulsed eximer laser was used to melt particles and propel the liquid to a substrate. On the left is a superconductor splat from these experiments, on the right is an alumina splat.

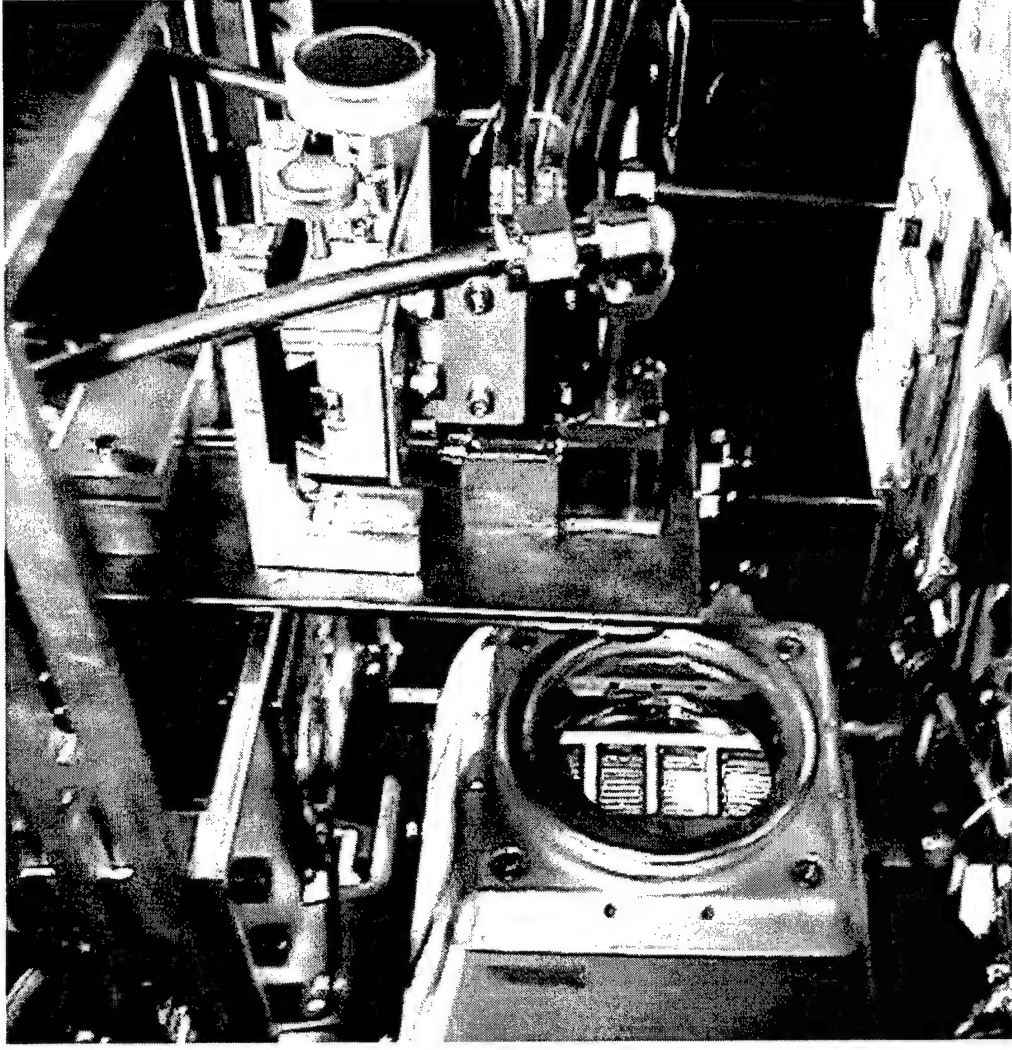
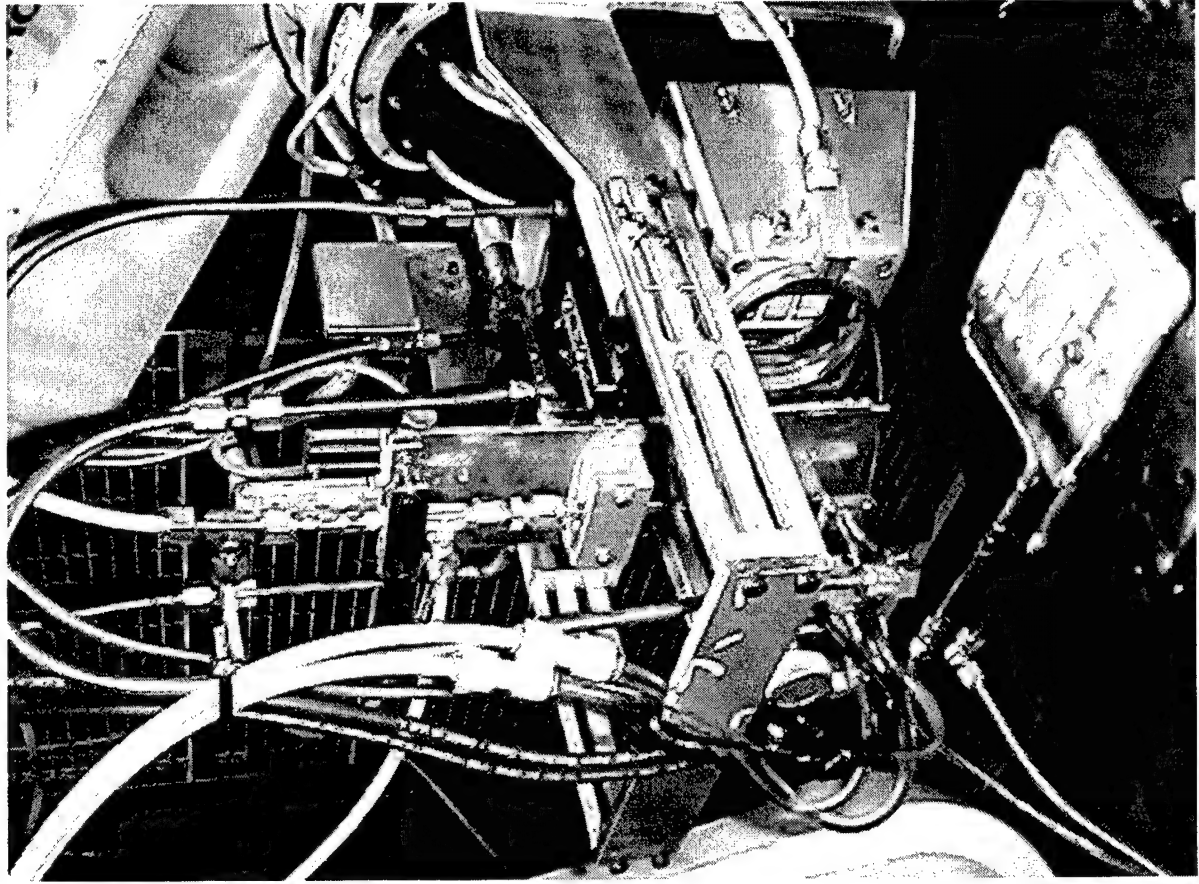


A superconductor splat on a polycrystalline substrate was placed in the finely focused ion beam apparatus and trimmed to a 5 micron disk as shown on the right.





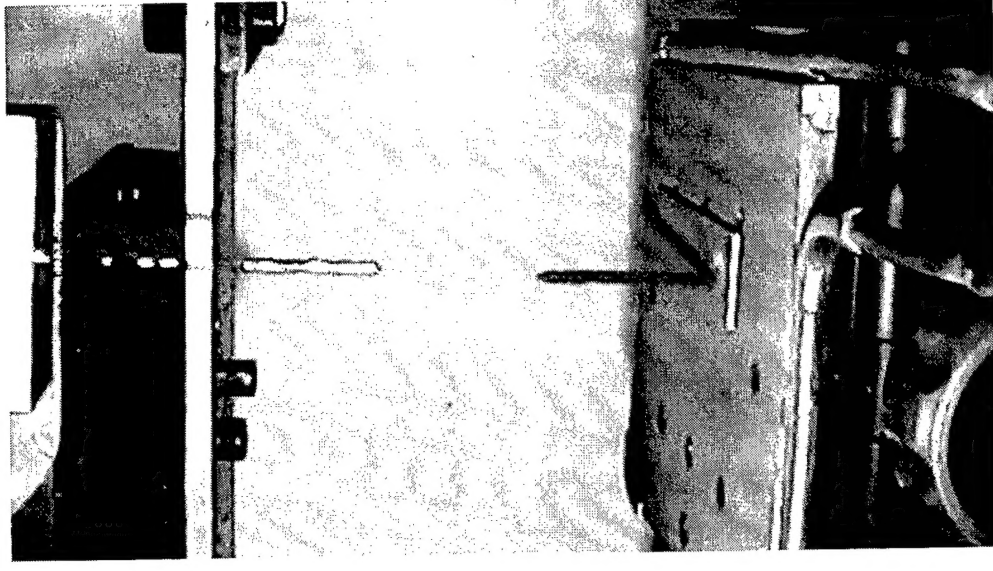
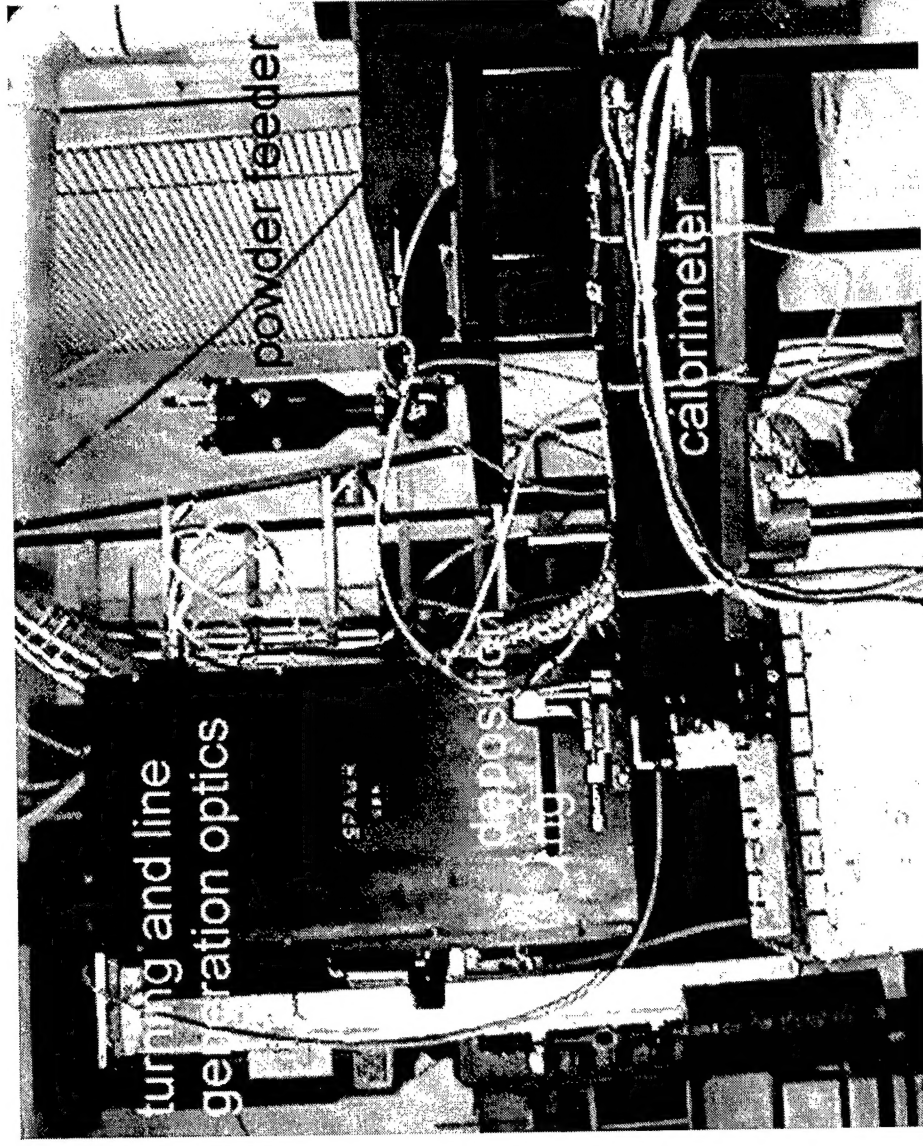
# *Diode preheat experiments*



Diode preheat and reflector on main  
Laser beam. Nuvonyx exps. Nov. 2000

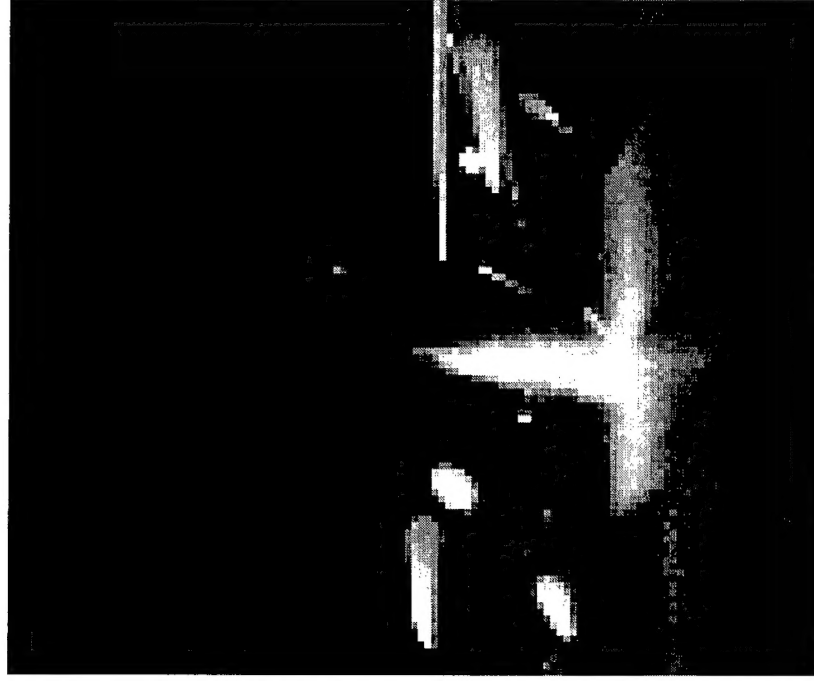


# *Experiments at UTSI*



UTSI CO<sub>2</sub> laser measured output was 2300 W. A sintered needle of alumina was built by indexing the laser in the z direction.

# *Alumina weld from UTSI*



[Click on picture to view movie](#)

Alumina powders were melted in flight and the substrate rastered to form a weld on the alumina substrates. The deposit was a collection of sintered spheres and not 100% dense.

# *Tasks accomplished*

- Powders
  - Various  $\text{Al}_2\text{O}_3$ , 96%-100%, coated and uncoated
  - Mullite
  - High Temperature Superconductors (Y-Nd 123)
- Nozzles
  - Laminar flow and co-flow
  - Measured velocity and divergence by collection and imaging
- Image furnace calculation strategy
- Models and Simulations
  - Newtonian simulator
  - Need to consider gradients,  $\alpha(T)$ , particle stream density
- Melting experiments
  - 810 nm Nuvonyx diode source
  - $\text{CO}_2$  laser at UTSI
  - Pulsed eximer laser

## *summary*

- Melting and deposition of a stream of ceramic powders is feasible. High temperature refractories will require more than 4 kW of power for good deposits.
- Considerable scientific and engineering challenges remain on the path to a viable process.